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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

**EXPEDITE**

FEB 29 1984

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCE

MEMORANDUM

SUBJECT: Requirements for Methyl Bromide tolerances.

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Hazard Evaluation Division (TS-769)

THRU: Charles L. Trichilo, Chief  
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TO: William Miller, PM. No. 16  
Registration Division (TS-767)  
and  
Toxicology Branch  
Hazard Evaluation Division (TS-769)

Residue Chemistry Branch was requested to provide an expedited evaluation of the data requirements for the establishment of tolerances for residues of methyl bromide, per se, resulting from the currently registered fumigation uses. (See Douglas Campt's memo of 1/1/84).

Conclusions

- 1a. The fate of methyl bromide in fumigated commodities has not been adequately delineated. Appropriate radiolabeled metabolism/degradation studies are needed to determine the portion of the applied methyl bromide that dissipates vs the portion that reacts with the treated commodity. Further, the nature of the reaction products will have to be delineated to assess their toxicological significance.
- 1b. If significant levels of methyl bromide, per se, or any metabolites of toxicological concern persist in treated commodities appropriate radiolabeled animal metabolism studies will also be needed.

- 1c. Bromide ion has historically been considered the residue of concern for methyl bromide. Toxicology Branch should be consulted concerning whether bromide ion should continue to be regulated.
2. No analytical methodology has been demonstrated to be suitable for the enforcement of tolerances for methyl bromide, per se. The development of methods to determine the levels of methyl bromide per se, in the wide variety of commodities for which its use is currently registered will also be needed before tolerances could be granted.
3. RCB does not consider the available residue data adequate to determine the levels of methyl bromide, per se, likely to remain in treated commodities. The development of appropriate residue data using validated analytical methodology to determine the levels of residues that remain in treated commodities for up to a week after fumigation will also be needed to determine the appropriate tolerances levels.
4. RCB can draw no conclusions concerning the possibility of secondary residues of methyl bromide, per se, in meat, milk, poultry or eggs until the questions regarding the nature and level of the residues that result in treated commodities have been resolved. If methyl bromide, per se, or metabolites of concern to Toxicology Branch are found then conventional ruminant and poultry feeding studies will also be required.
5. The inclusion of chloropicrin in many of the methyl bromide formulations poses question about possible residues of this compound remaining treated commodities. Although Section 40CFR 180.199 in or on currently states that no residues of chloropicrin will remain in the treated commodity, it is RCB's opinion that this conclusion and the exemption of chloropicrin from the requirement of a tolerance under Section 40CFR 180.1008 should be reconsidered.

### Detailed Considerations

#### Formulations

A variety of formulations of methyl bromide are currently registered. Methyl bromide accounts for 98% of most of the formulations; however, some of the formulations contain as little as 43% methyl bromide. For essentially all for the formulations the remainder is chloropicrin. Several of the available labels also list an "inert" ingredient at less than 1% by weight. No confidential statements of formula have been provided..

Chloropicrin has been exempted from the requirement of a tolerance when used as a fumigant after harvest on barley, corn, oats, popcorn, rice, rye, sorghum and wheat. Chloropicrin is also registered for use in combination with methyl bromide when used as a soil fumigant. Section 40CFR 180.199 states that no tolerance for residues of chloropicrin are established since no residues remain after the soil fumigation use.

### Proposed Use

Methyl bromide is currently registered as a soil fumigant, a post-harvest commodity fumigant and as a fumigant in the USDA's Plant Protection Quarantine program.

It is currently registered for post-harvest fumigations of the following commodities:

|                 |                      |               |
|-----------------|----------------------|---------------|
| Alfalfa         | Garlic               | Potatoes      |
| Barley          | Grapes               | Pumpkins      |
| Beans           | Horseradish          | Radishes      |
| Beets           | Jerusalem artichokes | Rice          |
| Cabbage         | Melons               | Rutabagas     |
| Carrots         | Nuts                 | Rye           |
| Chestnuts       | Oats                 | Salsify       |
| Cipollini bulbs | Okra                 | Sorghum       |
| Citrus fruits   | Onions               | Spices        |
| Cocoa beans     | Parsnips             | Squash        |
| Copra           | Peanuts              | Stone fruit   |
| Corn            | Peas                 | Sugar beets   |
| Cottonseed      | Peppers              | Sweet corn    |
| Cucumbers       | Pimentoes            | Sweetpotatoes |
| Dates           | Pineapples           | Turnips       |
| Eggplants       | Pome fruits          | Wheat         |
| Figs            | Popcorn              | Yams          |

Application rates range from 1 to 6 lbs. act./1000 cu. ft. of storage area. This rate corresponds to an initial concentration of approximately 20 to 125 ppm in the treated commodity, assuming a completely even distribution of the methyl bromide.

Chloropicrin may be applied to grains in storage at rates up to 6 lbs. act./1000 bu. No aeration period is required and there is no limit on the number of applications. The single application rate corresponds to an initial level of approximately 100 ppm in the treated grain assuming a completely even distribution of the chloropicrin.

Soil fumigation uses of methyl bromide at rates of up to 1000 lbs. act./acre are currently registered. These use are currently limited to either non-crop or pre-transplant uses with the exception of strawberries.

Chloropicrin may be applied to any crop as preplant soil fumigant at rates up to 1021 lbs. act./acre. A seven day minimum aeration interval is required before planting.

The treatment of agricultural premises, boxes and crates for harvesting or storing raw agricultural commodities have also been registered.

#### Nature of the Residue

No radiolabeled metabolism studies investigating the fate of methyl bromide when applied to stored commodities are currently available. Such studies are needed to determine the portion of the applied methyl bromide that dissipates vs the portion that reacts with the treated commodity. Further, the nature of the reaction products will have to be delineated to assess their toxicological significance.

If significant levels of methyl bromide, per se, or any metabolites of toxicological concern persist in treated commodities appropriate radiolabeled animal metabolism studies will also be needed.

No final conclusions regarding methodology, residue data, appropriate tolerance levels or the possible need for animal feeding studies can be drawn until the fate of methyl bromide has been adequately delineated.

#### Analytical Methods

The PAM II method for inorganic bromides has been accepted for enforcement of inorganic bromide tolerances. RCB has no reason to believe that the procedure would not be suitable for the determination of inorganic bromides in or on treated commodities.

An electron capture gas chromatographic procedure (that of J. R. King, et. al. "Residues of Methyl Bromide in Fumigated Grapefruit Determined by a Rapid Headspace Assay." J. Agric. Food Chem. 1981, 29, 1003) is available. The procedure involves grinding a 50g. sample with distilled water in a sealed container, sampling the the headspace gases and analysis by GLC. The procedure is reported to be sensitive to 2 ppb in grapefruit.

Procedures to determine methyl bromide (organic bromides) by difference from the total bromide level are also available; these procedures will not provide the required sensitivity.

It is our understanding that FDA is also developing methodology for the determination of methyl bromide. However, before RCB can consider any procedure adequate for tolerance enforcement, a successful method trial must be conducted.

### Residue Data

The available data reflecting residue levels of methyl bromide, per se, in treated commodities are extremely limited. Data are only available for blueberries, lentiles, onions, pears, prickly pear, tea, various spices, and yams.

For much of the data that is available, there are no validation data to confirm method sensitivity or recovery.

The procedures used are generally reported to be sensitive to 10 to 20 ppb. Residues immediately after treatment ranged as high as 150,000 ppb. With the exception of one sample of pears, which contained residues of 40 ppb at 48 hours, no detectable residues were found 24 hours after treatment.

Although the data indicate that residues of methyl bromide, per se, decline rapidly after application on the various commodities RCB can make no determination as to the expected residue levels in treated commodities following methyl bromide fumigations.

Appropriate controlled studies that determine the residue levels resulting on a representative number of commodities from fumigation at the maximum recommended rates by validated analytical methodology will be needed to establish any tolerances for residues of methyl bromide, per se.

### Meat, Milk, Poultry and Eggs

Although at this time RCB considers secondary residues of methyl bromide, per se, unlikely in meat, milk, poultry or eggs RCB can make no final determination until the questions regarding the nature and level of the residues and the required analytical methodology have been resolved. If significant residues of methyl bromide, per se, or any metabolites of concern occur in feeds, conventional ruminant and poultry feeding studies may also be needed.

cc: Reading file  
Circu  
Reviewer  
Methyl bromide S.F.  
TOX

TS-769:Reviewer:JMWorthington:Date:2/24/84  
RDI:Section Head:ARR:Date:2/27/84:RDS:Date:2/28/84

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